Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

January 1, 2004 – March 31, 2004

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Cooperative Agreement No: DE-FC26-04NT41992

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT41992, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period January 1, 2004 through March 31, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being cofunded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites to provide longer-term catalyst life data. Pilot-scale wet FGD tests will be conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system will also be used downstream of catalysts currently being tested as part of another cooperative agreement (DE-FC26-01NT41185). The catalyst pilot units to be used on project 41992 are currently in use on project 41185; pilot catalyst testing on project 41992 will commence after the catalyst tests for project 41185 are completed.

This is the first reporting period for the subject Cooperative Agreement. During this period, project efforts included initial project planning, commencing the design and fabrication of the pilot wet FGD system, and a site kickoff meeting at the TXU Energy host site, their Monticello Station. Laboratory testing began to determine the activity of candidate catalysts at simulated Monticello Plant conditions. Finally, a meeting was held at the site of the planned manufacturer for a carbon-based catalyst that will likely be tested at Monticello, to discuss logistics for preparing the experimental catalyst in pilot quantities.

This Technical Progress Report describes the design of the pilot wet FGD system and results of the laboratory tests completed to date; there is no additional technical progress to report.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period January 1, 2004 through March 31, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

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Four utility team members are providing project host sites for testing. GRE is providing a test site at their Coal Creek Station (CCS), which fires a North Dakota lignite. City Public Service of San Antonio (CPS) is providing a test site at their J.K. Spruce Plant, which fires a Powder River Basin (PRB) subbituminous coal. Both CCS and Spruce are currently hosting mercury oxidation catalyst pilot tests as part of project 41185. They will also host pilot FGD tests downstream of the catalysts as part of the current, 41992 project.

For the current project, TXU will be hosting pilot catalyst tests and intermittent wet FGD pilot tests at their Monticello Station, which fires a Texas lignite/Power River Basin (PRB) coal blend. The TXU test program will commence after the current testing at CCS is completed the spring of 2004. Duke Energy will also host oxidation catalyst pilot and wet FGD pilot tests, at one of their sites firing a low-sulfur Eastern bituminous coal. The Duke Energy tests will commence after the current testing at Spruce is completed at the end of calendar year 2004.

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, January 1, 2004 through March 31, 2004, is the first full technical progress report period for the project. Efforts over the current period included initial project planning, commencing the design and fabrication of the pilot wet FGD system, and conducting a site kickoff meeting at the TXU Energy host site, their Monticello Station. Laboratory testing began to determine the activity of candidate catalysts at simulated Monticello conditions. Finally, a meeting was held at the site of the planned manufacturer for a carbon-based catalyst that will likely be tested at Monticello to discuss the logistics or preparing the experimental catalyst in pilot quantities.

One subcontract was issued during the current reporting period, to Capco, Inc. of Kilgore, Texas, for fabrication of the alloy wet FGD absorber vessel and associated items.

Problems Encountered

There were no significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (April 1 through June 30, 2004), pilot-scale wet FGD tests will be conducted downstream of oxidation catalysts being operated at CCS as part of another DOE-funded project (DE-FC26-01NT41185), to determine how effectively the catalytically oxidized mercury will be scrubbed. The catalyst pilot unit at CCS will be shut down after the wet FGD tests are completed, and that pilot unit will be shipped to Monticello, where plant staff will install it adjacent to the 3C induced draft (ID) fan on Unit 3.

Prospects for Future Progress

During the next reporting period (July 1 through September 30, 2004), catalyst testing will commence at the Monticello site. Catalysts will be evaluated for elemental mercury oxidation activity through routine (~monthly to bimonthly) evaluation trips. Intensive gas characterization efforts and initial wet FGD pilot testing should also occur during the quarter.

At CPS’ Spruce Plant, pilot wet FGD tests should be conducted during the quarter. Catalysts will be evaluated for elemental mercury oxidation activity as part of the previous project (41185) through the end of the calendar year.

EXPERIMENTAL

The work being conducted as part of this project will use three different experimental apparatus types. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated), the first of which is currently located at GRE's CCS Station in North Dakota. A second, nearly identical pilot unit is currently located at CPS' Spruce Plant. During the course of this project, these two pilot units will be relocated and installed at TXU Energy's Monticello Plant and at a Duke Energy plant, respectively.

Each pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports as part of the ongoing 41185 project[1,2, 3, 4]. The activity of these catalysts is determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst samples under simulated flue gas conditions. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports for the 41185 project[3, 4].

The third experimental apparatus is a pilot-scale wet FGD unit that is being designed and fabricated as part of the current, 41992 project, to allow the measurement of how effectively catalytically oxidized mercury can be scrubbed. The design is well underway, and many of the components have been procured. The pilot unit is being designed to treat the flue gas from one of four catalyst chambers on the mercury oxidation catalyst pilot unit. The design basis for the pilot wet FGD system is summarized in Table 1 below. Figure 1 is a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system.

Table 1. Pilot-scale Wet FGD Design Basis

Design Feature	Value
Gas Conditions:	
Flue Gas flow rate	2000 acfm
Inlet SO_2 concentration	2000 ppmv max, 1000 ppm or less normal
Inlet temperature	300°F
Design SO_2 removal percentage	~95% (varies with inlet SO_2, reagent ratio, LS grind, chloride concentration in slurry liquor)

Table 1 (continued)

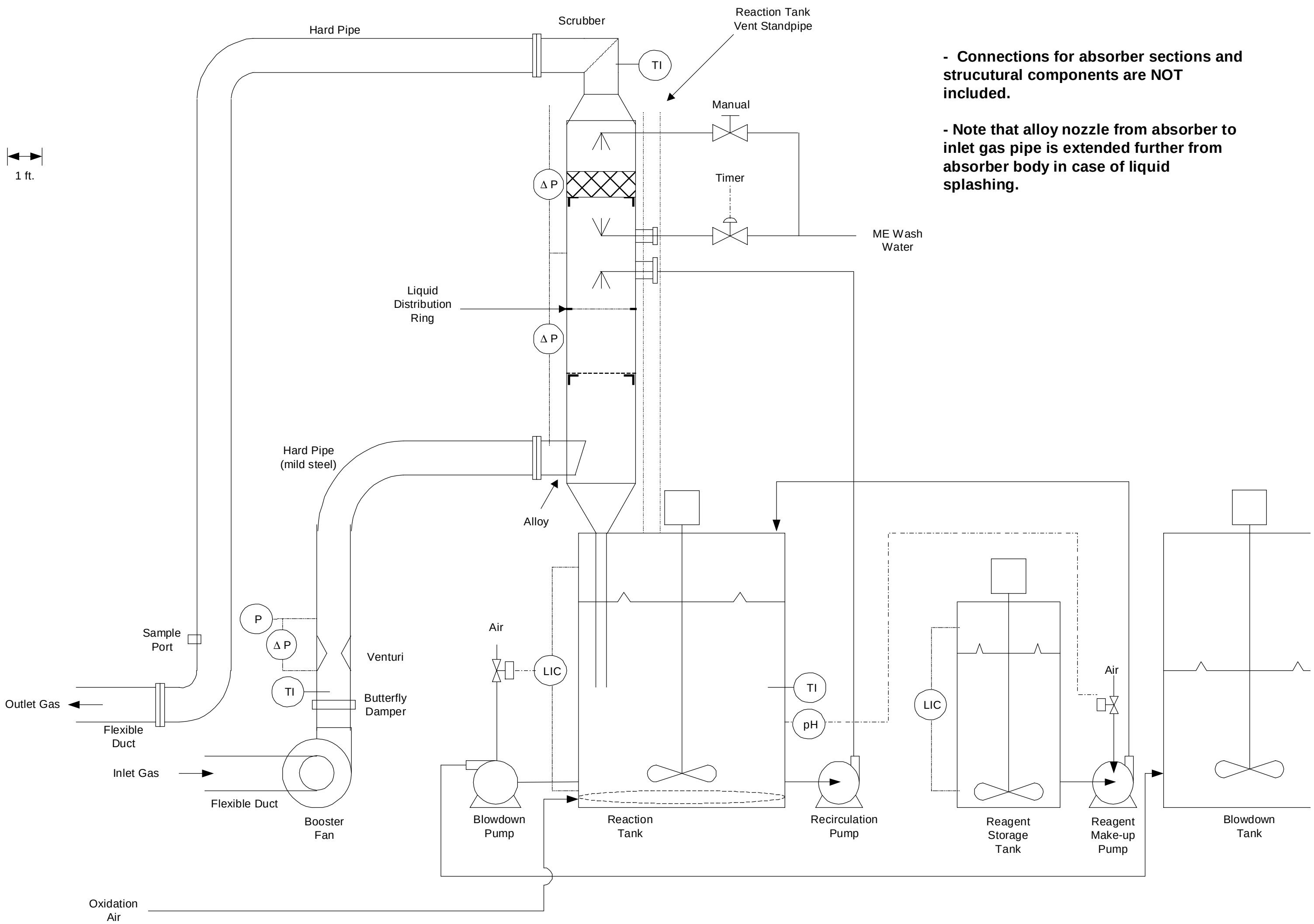
Design Feature	**Value**
Scrubber Design Criteria:	
Contactor type	Spray/tray
Flue gas inlet ductwork (including venturi, butterfly control valve)	10-in.
Booster fan sizing	2000 acfm at 14-in. H_2O differential
Flue gas inlet duct velocity	60 ft/s
Flue gas velocity in absorber inlet nozzle	24 ft/s
Inlet nozzle diameter	16-in.
Flue gas velocity through absorber	8.4 ft/s
Absorber diameter	24-in.
Tray open area	24%
Tray hole diameter	1.375 in.
Recycle slurry rate	200 gpm max
L/G ratio	127 gal/kacf
Slurry nozzle	BETE MP 1625M, 3-in., 90^o full cone, 10 psig
Mist eliminator type	Single stage, Koch Otto York, Style VIII-3-1.5
ME wash rate	1.5 gpm/ft^2/level
ME wash levels	2 (front and back side)
ME nozzle type	90^o full cone, 40 psig
Outlet duct velocity	48 ft/s
Oxidation air rate, max O/SO_2 ratio	10 at 2000 ppmv inlet SO_2
Tank Sizing:	
Reaction tank dimensions	6-ft diameter x 8-ft high, covered, baffled, single top entry agitator
Reaction tank solids residence time	18-hr at 2000 ppmv inlet SO_2, 35-hr at 1000 ppmv
Reaction tank liquid holdup, minimum	7.4 minutes
Reagent tank dimensions	3 ft-diameter x 6-ft high, open top, baffled, single top entry agitator
Reagent tank storage capacity, hrs supply	14-hr at 2000 ppmv inlet SO_2, 27-hr at 1000 ppmv
Blow down tank dimensions	5 ft-diameter x 8-ft high, open top, baffled, single top entry agitator
Blow down tank storage capacity, hrs of FGD operation	13-hr at 2000 ppmv inlet SO_2, 25-hr at 1000 ppmv

Table 1 (continued)

Design Feature	Value
Piping Design:	
Recycle slurry pipe diameter	3-in. flex hose
Recycle slurry pipe velocity, max	9.1 ft/s
All other piping (reagent make-up, slurry blow down, ME wash water)	0.5-in. flex hose
Materials of Construction:	
Inlet ductwork, to fan	Stainless steel lined flexible duct
Inlet ductwork, fan to absorber inlet nozzle	Carbon steel
Absorber vessel, inlet nozzle to outlet nozzle, including tray	254-SMO solid alloy
Absorber maximum chloride concentration	23,000 ppm (very conservative), 28,000 ppm (conservative)
Recycle slurry nozzle	Cobalt alloy, Stellite #6
Mist eliminator	Polysulfone, with FRP nuts and bolts
Absorber outlet duct, to edge of skid	254-SMO solid alloy
Outlet ductwork, from edge of skid	Stainless steel lined flexible duct
Reaction tank, reagent tank, blow down tank	Carbon steel lined with vinyl ester
Reaction tank agitator impeller and shaft	254-SMO solid alloy, Pro-Quip
Reagent tank agitator impeller and shaft	Carbon steel (possibly rubber lined), Pro-Quip brand
Blow down tank agitator and shaft	Carbon steel (have 4 used agitators available for reuse), Pro-Quip brand
Recycle slurry pump	Rubber-lined iron, Weir (Warman)
Reagent makeup pump, slurry blow down pump	Plastic diaphragm pump (PET), Wilden
Instrumentation:	
Flow rate	Inlet flue gas venturi
Temperature	Inlet flue gas, outlet flue gas, reaction tank slurry
Pressure	Inlet flue gas, recycle slurry, oxidation air
Pressure drop	Gas flow rate venturi, absorber spray/tray section, absorber ME section
Level	Reaction tank, reagent tank, blow down tank
pH	Reaction tank slurry
Mercury concentration	Absorber inlet/outlet sample ports, solenoid valves, heat-traced tubing and IGS filter

Table 1 (continued)

Design Feature	Value
Control Strategies:	
Flue gas flow rate	PID controller to control butterfly valve position based on feedback from venturi meter pressure differential
Reaction tank pH	On-off control of air-drive reagent feed pump based on feedback from reaction tank slurry pH meter
Reaction tank, reagent tank, blow down tank	Manual control based on level indication, high and low level alarms
Absorber outlet temperature	Fan trip on high temperature to protect ME
Recycle slurry flow	Manual control based on slurry feed pressure to nozzle, SO_2 removal performance (as measured by gas indicating tubes); pump trip on low-low level in reaction tank



- Connections for absorber sections and strucutural components are NOT included.

- Note that alloy nozzle from absorber to inlet gas pipe is extended further from absorber body in case of liquid splashing.

Figure 1. Simplified P&ID for Pilot Wet FGD System

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, January 1, 2004 through March 31, 2004. Results to date have been limited to initial laboratory activity screening of candidate catalyst materials for the upcoming pilot tests.

Laboratory Evaluation of Candidate Catalysts

Laboratory evaluation of candidate catalyst materials at simulated Monticello Station Unit 3 conditions began during the current quarter. Three catalyst materials were evaluated: a selective catalytic reduction (SCR) catalyst from Mitsubishi Heavy Industries; a sample of palladium on alumina (Pd #1) prepared by Johnson Matthey, a new supplier being considered for supply of the catalysts for Monticello; and a sample of the carbon-based (C #6) material from the production run to make the catalyst currently being tested at Coal Creek Station as part of project 41185.

Table 2 shows the simulation gas species concentrations, and Table 3 and Figure 2 show the results of tests conducted through the end of March. All of the results shown are based on the use of “Tris” solutions (rather than KCl solutions) in the Hg analyzer impinger train when measuring elemental mercury concentrations downstream of the catalysts. The results show similar activity for all three catalyst types when plotted as a function of area velocity (in standard ft/hr); a single line would appear to reasonably fit the data for all three catalyst types. However, the C #6 sample was tested at relatively low area velocity values, so there is no overlap between the area velocities tested for the C #6 and MHI catalysts. Testing during the current quarter will include retesting the Coal Creek C #6 material at higher area velocities and testing samples of the materials currently being tested at Spruce Plant as part of project 41185. These include a sample from the second batch of C #6 material (prepared for the Spruce pilot), SCR catalyst from Argillon, Pd #1 from Sud-Chemie Prototech, and gold on alumina from Sud-Chemie Prototech.

Table 2. Target Simulation Gas Composition for Monticello Laboratory Tests

Species	Concentration
Hg^0	45-57 $\mu g/Nm^3$
SO_2	600 ppmv
HCl	1 ppmv
NO_X	400 ppmv
H_2O	15%
CO_2	12%
O_2	6%
N_2	Balance

Table 3. Laboratory Catalyst Activity Test Results Through March 2004

Catalyst, core length	Core Length, in.	Cell Pitch, cpsi	No. of Cells in Core	Flow Rate, L/min	Area Velocity, sft/hr	Hg Concentration (mg/Nm^3) Inlet Total	Hg Concentration (mg/Nm^3) Outlet Hg^0	Hg^0 Oxidation, %
MHI SCR	0.97	47	8	0.61	46	48.9	9.61	80
MHI SCR	0.97	47	8	0.93	70	50.2	6.55	87
MHI SCR	0.97	47	8	1.44	109	45.9	11.8	74
C #6, 2002 production	2.25	77	14	0.61	14	57.0	0.65	99
C #6, 2002 production	2.25	77	14	0.93	22	55.0	5.99	89
C #6, 2002 production	2.25	77	14	1.44	34	53.1	1.31	98
Johnson Matthey Pd #1	1.25	64	13.5	0.61	24	54.6	2.62	95
Johnson Matthey Pd #1	1.25	64	13.5	0.93	36	49.3	3.06	94
Johnson Matthey Pd #1	1.25	64	13.5	1.44	57	44.5	5.68	87

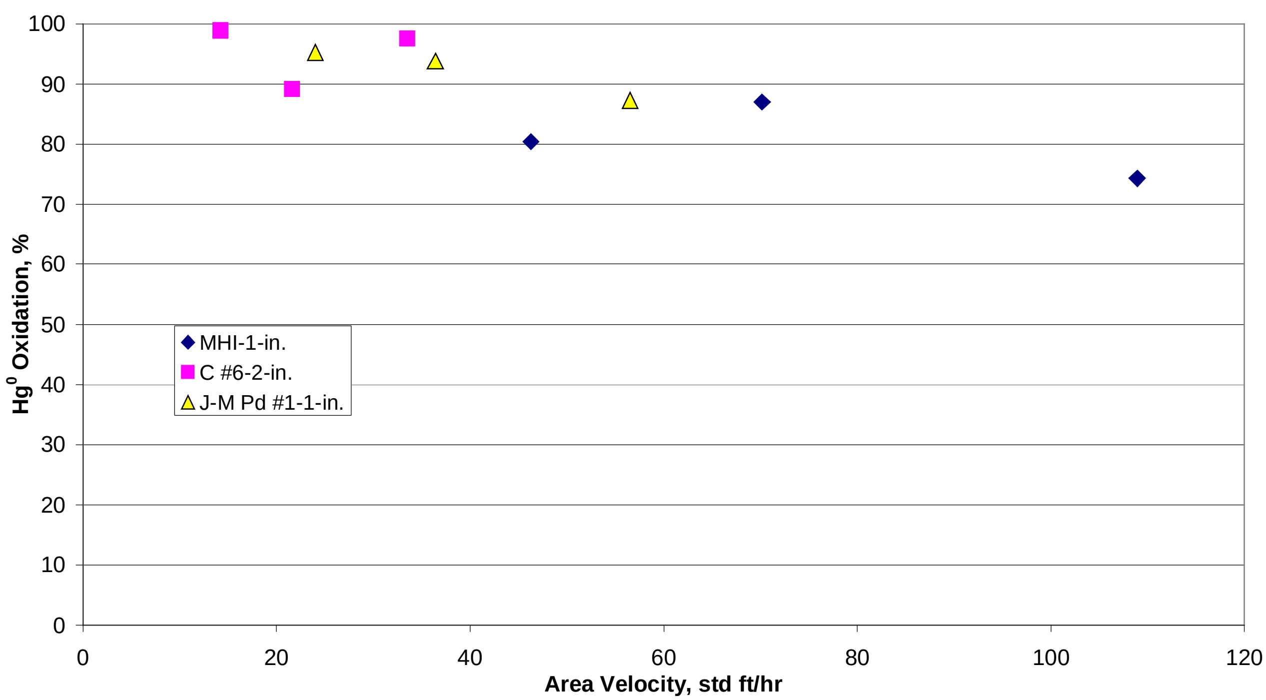


Figure 2. Catalyst Hg^0 Oxidation Activity at Simulated Monticello Plant Gas Conditions

CONCLUSION

Because this report covers only the first quarter of the project, few technical results have been generated. Only nine laboratory catalyst screening tests have been conducted as part of the project, while many more are planned prior to catalyst selection for the pilot catalyst tests at Monticello. Consequently there are no conclusions that can be made at this time.

REFERENCES

1. Blythe, Gary M. “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” Quarterly Technical Progress Report, October 1, 2002 – December 31, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. January 2003.

2. Blythe, Gary M. “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” Quarterly Technical Progress Report, July 1, 2002 – September 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. October 2002.

3. Blythe, Gary M. “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” Quarterly Technical Progress Report, March 1, 2002 – June 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. July 2002.

4. Blythe, Gary M. “Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems,” Quarterly Technical Progress Report, January 1, 2002 – March 31, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. April 2002.

5. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems, Final Report, Phase II,* U.S. Department of Energy Cooperative Agreement Number DE-AC22-95PC95260, URS Corporation, Austin, Texas 78729. June 2001.